

# Development of a Nonchromate Structural Adhesive Bond Primer

---

Mark Jaworowski

UTRC

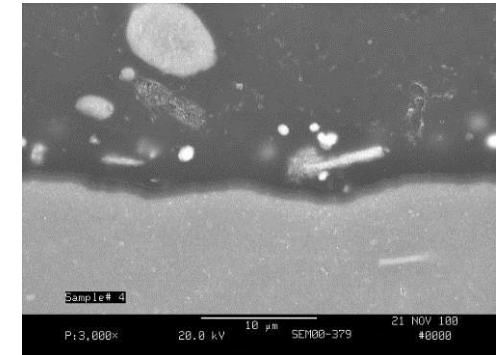
2014 AsetsDefense meeting

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE <b>NOV 2014</b>		2. REPORT TYPE		3. DATES COVERED <b>00-00-2014 to 00-00-2014</b>	
4. TITLE AND SUBTITLE <b>Development of a Nonchromate Structural Adhesive Bond Primer</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>United Technologies Research Center (UTRC),411 Silver Lane,East Hartford,CT,06108</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>ASETSDefense 2014: Sustainable Surface Engineering for Aerospace and Defense, 18-20 Nov 2014, Fort Myer, VA.</b>					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>Same as Report (SAR)</b>	18. NUMBER OF PAGES <b>9</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

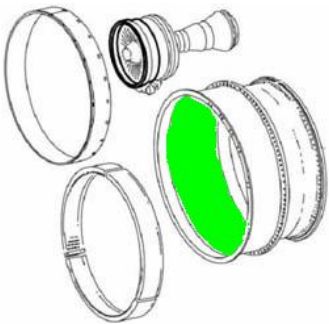
# Overview: Chromated Structural Adhesive Bond Primers

- Nominally 5 microns thick
- Prevent corrosion of base metal
- Applied to porous anodized surface
- Overcoated with non-inhibited epoxy adhesive
- High adhesive bond strength required for life of product
- Used in **load bearing applications** in **flight-critical** hardware
- Anodized surface / primer interface stability is critical
- Typically 5% or less  $\text{SrCrO}_4$  by weight as sprayed

Adhesive bond primer / anodize interface



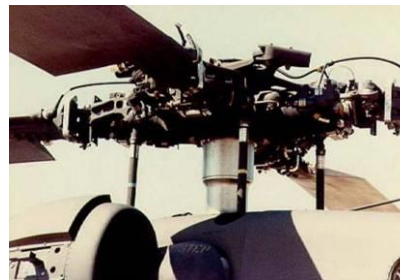
Fan Case Internal Bonding



All-composite propellers



Helicopter main rotor, blade pockets, swashplate



Engine nacelles  
Aerostructures



# Previous testing of chromate free adhesive bond primers

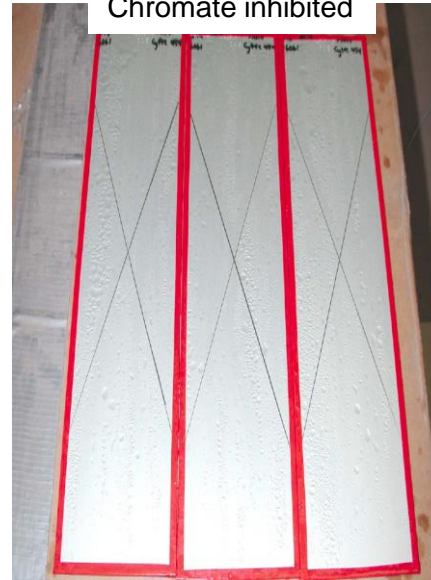
- Three companies (3M, Cytec, Henkel) produce aerospace structural adhesive bond primers
- Long-running surveillance of chromate-free alternatives by UTC companies shows weak corrosion inhibition

- (A) strontium chromate- inhibited bond primer, 2024 Al, 336 hours

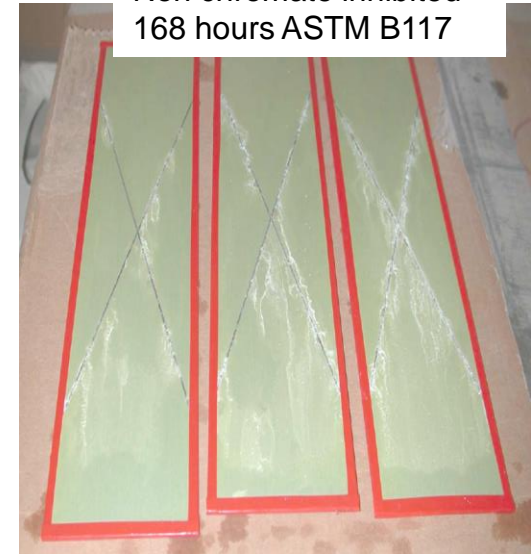
- (B) Cytec BR6700-1, 2024 Al, 168 hours

- Inhibition technology appears “low tech”: alkali silicate, zinc phosphate

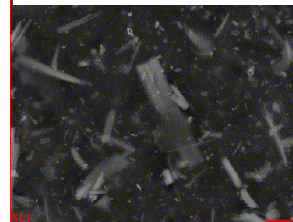
Chromate inhibited



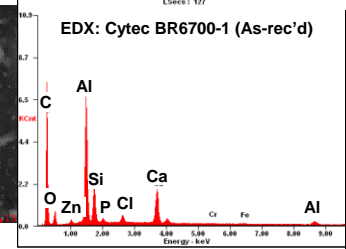
Non chromate inhibited  
168 hours ASTM B117



SEM: Cytec BR6700-1 (As-rec'd)

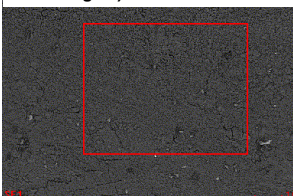


EDX: Cytec BR6700-1 (As-rec'd)

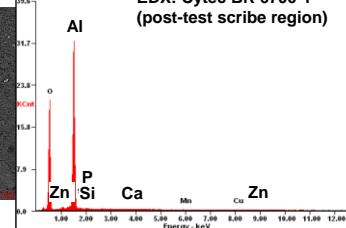


Cytec BR 6700-1 (As-rec'd)			
Element	At%	Atomic ratio	Possible component
AlK	3.92	43.56	Ca <sub>2</sub> SiO <sub>4</sub> , CaAlSiO <sub>3</sub> , ZnO
SiK	1.09	12.11	
PK	0.09	1.00	
ClK	0.17	1.89	
CaK	0.79	8.78	
ZnK	0.19	2.11	

SEM: Cytec BR 6700-1 (post-test scribe region)



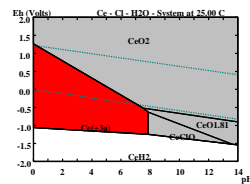
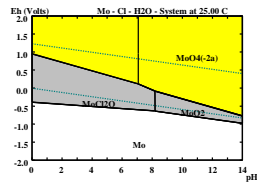
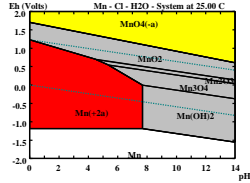
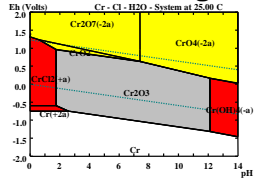
EDX: Cytec BR 6700-1 (post-test scribe region)



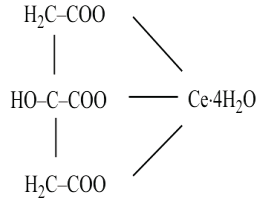
Cytec BR 6700-1 (post-test scribe region)			
Element	At%	Atomic ratio	Comment
AlK	33.14	552.33	Zn, P, Ca, and Si migrated
SiK	0.2	3.33	
PK	0.17	2.83	
CaK	0.09	1.50	
MnK	0.06	1.00	
CuK	0.24	4.00	
ZnK	0.21	3.50	

## Development timeline for UTC Chromate-Free Adhesive Bond Primer

## Nothing as good as Cr<sup>6+</sup>...



## Cerous citrate complex regulates solubility of multiple inhibitors



**Specification for engine use (EW-5000ET), testing of developmental sol gel compatible primer (EW-5005)**



1999 -2000:  
UTRC / P&W  
Development  
of Concept



2001-2002 –  
UTRC / P&W  
Joint  
Program  
Solubility  
Regulation

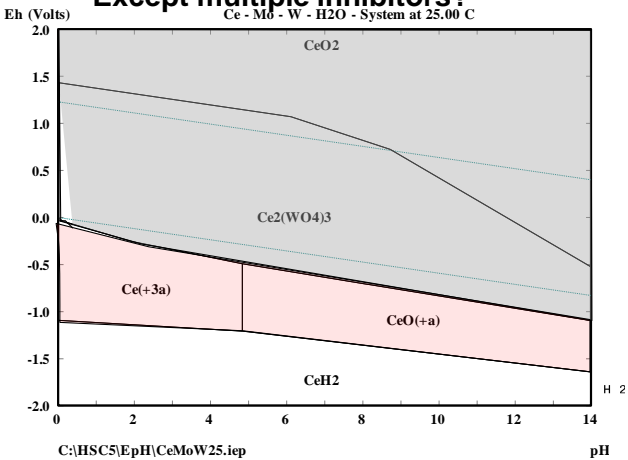


2006 UTRC  
Capability  
Project 7000-  
series AI  
Performance  
Improvement

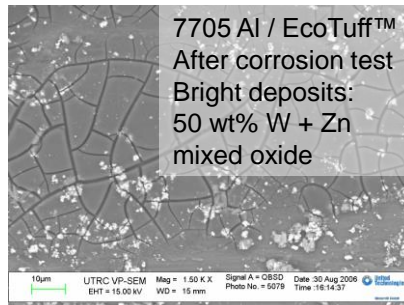


2009-2014  
UTRC /  
P&W/ 3M  
Product  
Development  
and  
Qualification

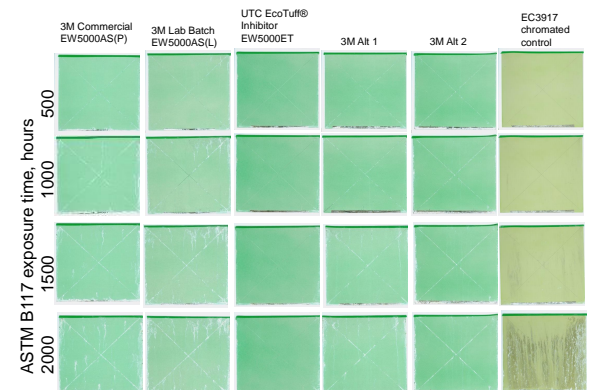
### Except multiple inhibitors?



## Optimized for multiple alloys



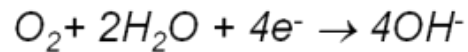
## Extensive corrosion and mechanical property testing



# Corrosion Science Model used to Develop Non Chromate Inhibitor

Corrosion involves at least two electrochemical reactions: Anodic (metal oxidation) and cathodic (i.e., oxygen reduction)

Cathodic sites



Anodic sites:  $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$

Anodic  $\rightarrow$  Cathodic ?

$\text{Al}_2\text{O}_3$  passive film

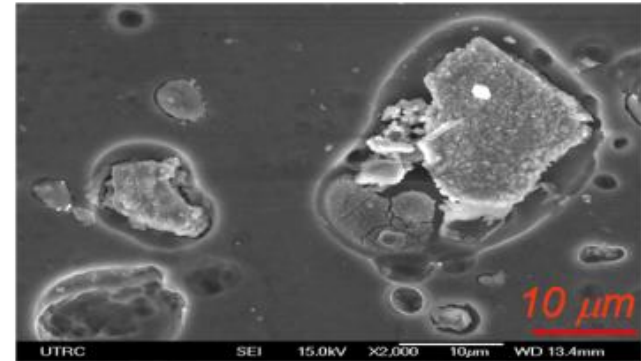
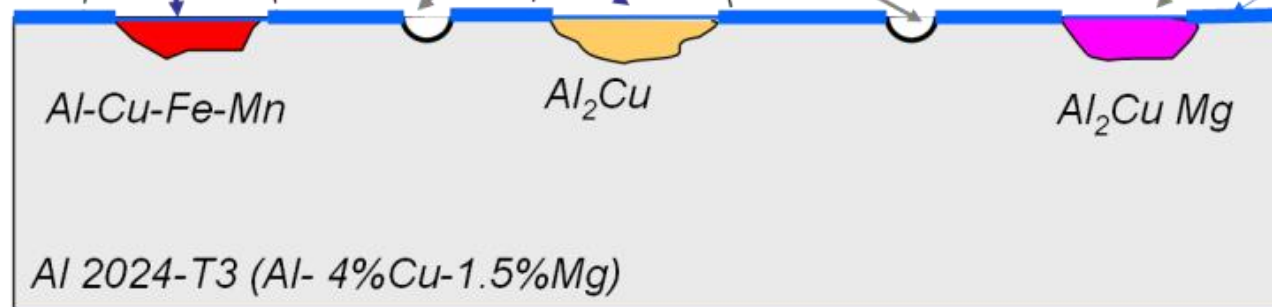


Fig.1 Corrosion of Al 2024-T3 in NaCl

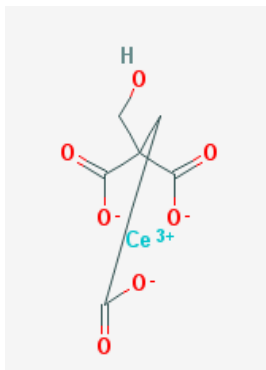
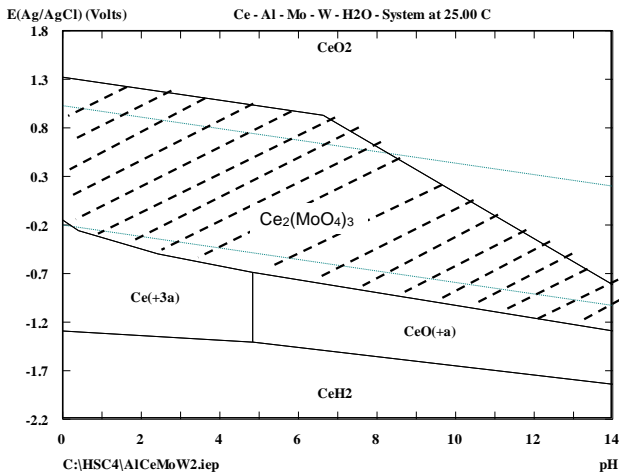
*An effective corrosion inhibitor system must demonstrate both anodic and cathodic inhibition in order to effectively prevent corrosion of Al alloys*



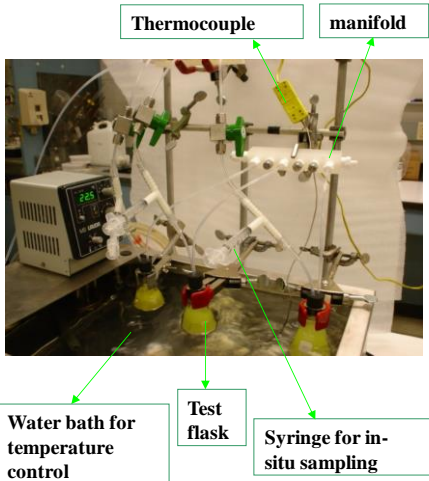
# Thermochemical Strategy for Multimode Inhibitor

Thermochemical identification of inhibition system

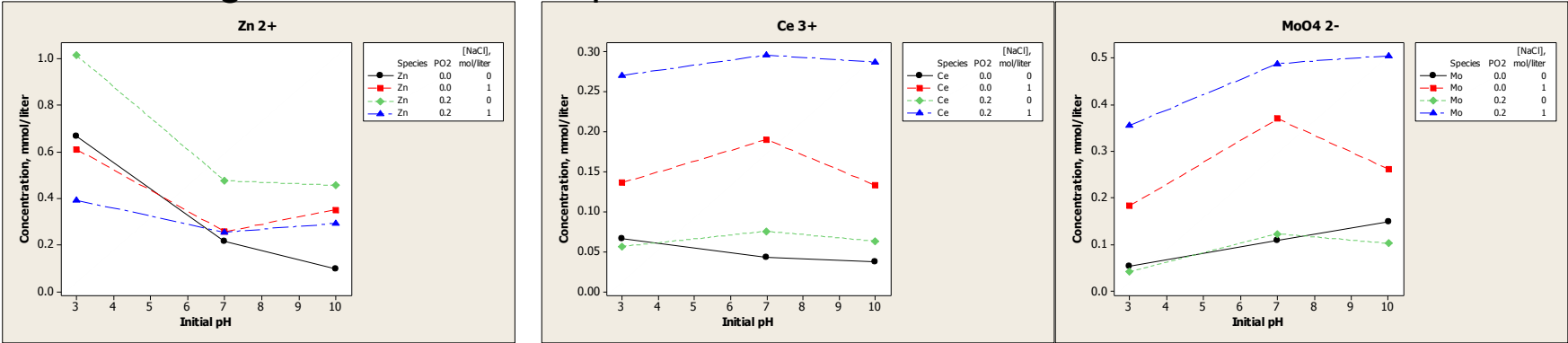
Cerous citrate chelation complex regulates solubility



Solubility test set-up

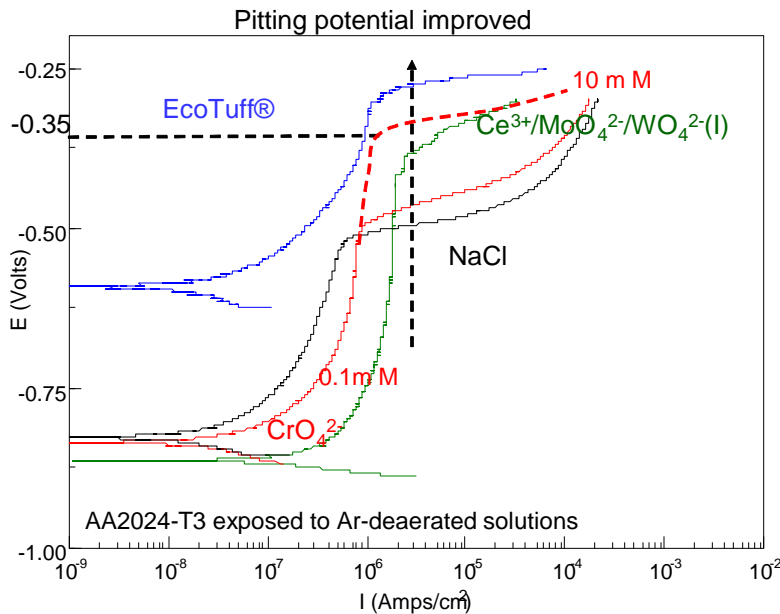


Target solubilities of separate corrosion inhibitor achieved

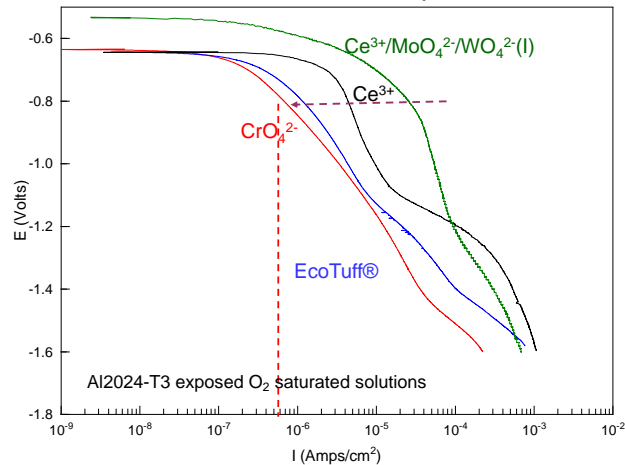


# Electrokinetic Confirmation of Active Inhibition in Coatings

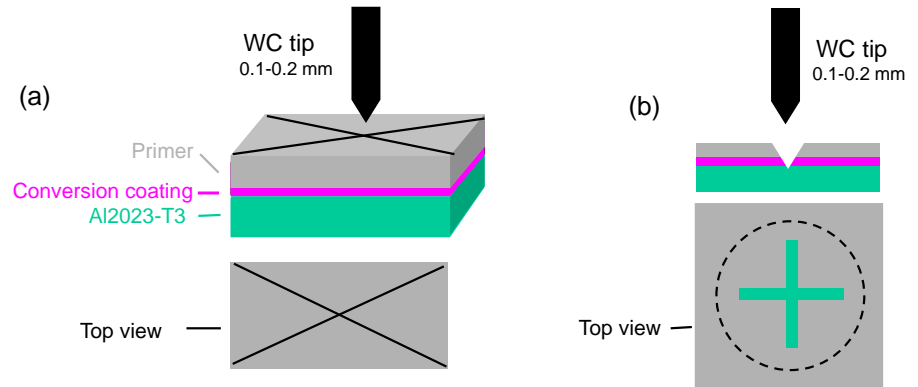
## Static DC Testing on Bare Al



## Cathodic inhibition comparable to Cr 6+



## Dynamic damage testing of trial primers

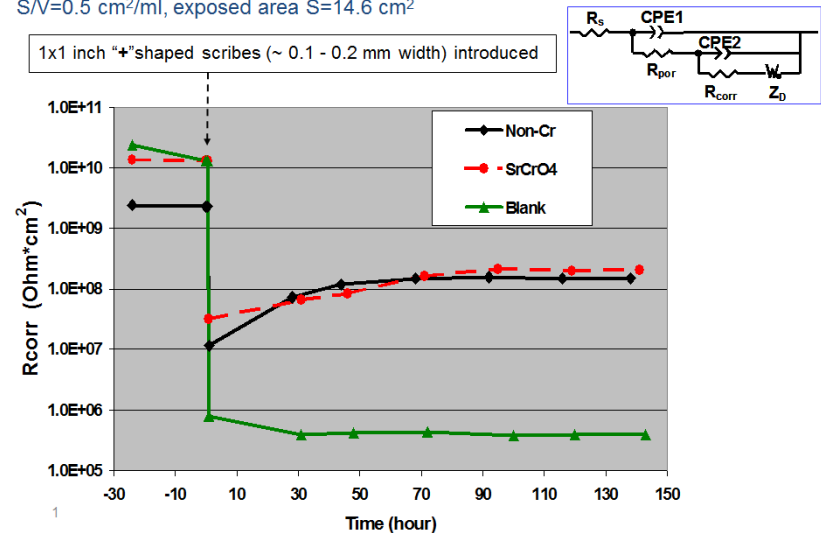


Schematic of defect production and samples for salt spray (a) and EIS test (b).

## EIS-Based Damage Resilience Test

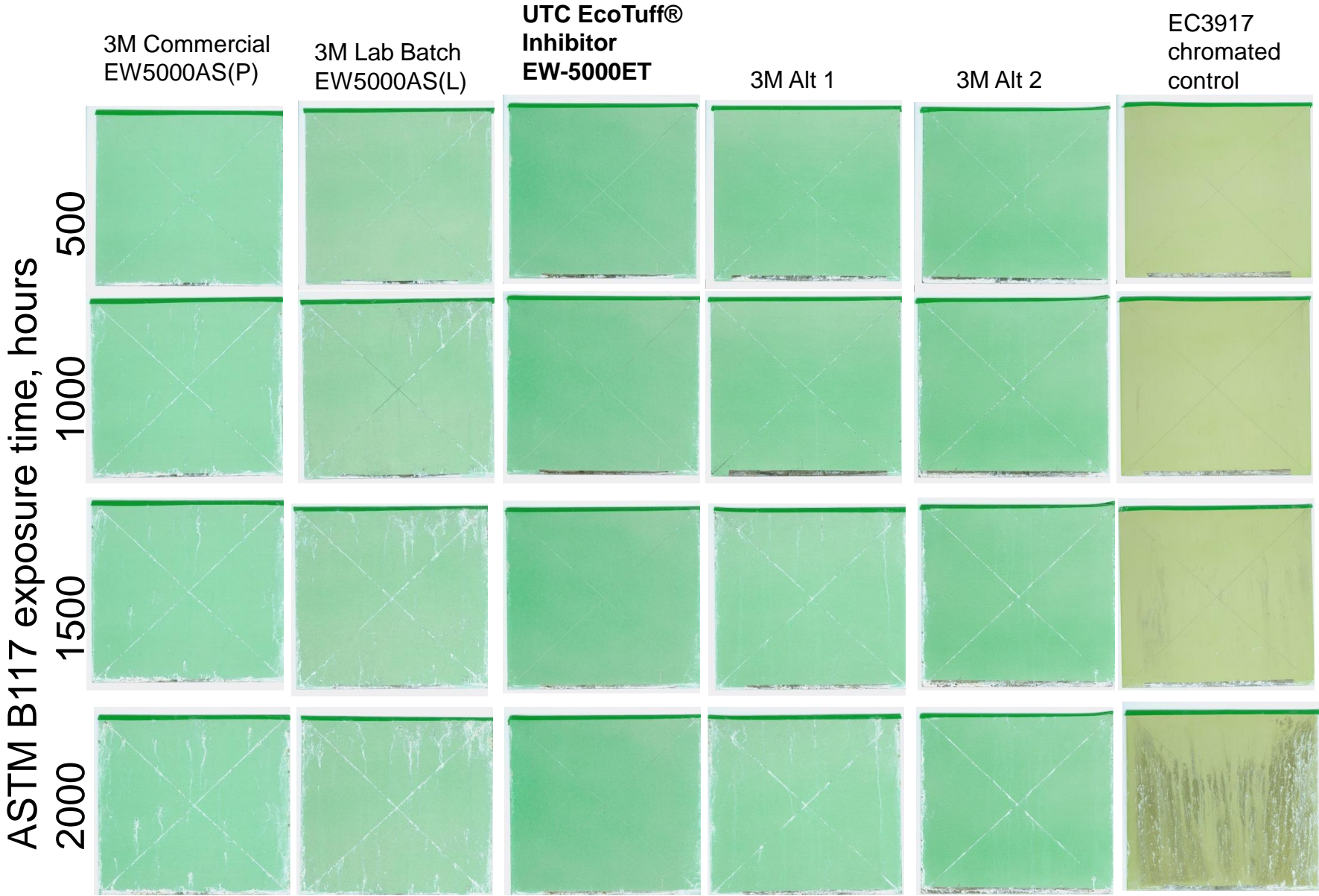
"Self-healing" is indicated for non-Cr inhibitors incorporated in epoxy primer

S/V=0.5 cm²/ml, exposed area S=14.6 cm²





# 3M / P&W / UTRC Corrosion Test Results PAA treated 2024-T3 Al



# 2014 R&D 100 Award to UTRC / P&W / 3M Team

## **Back row (L to R):**

Mark Jaworowski, UTRC, Michael Kryzman, UTRC

## **Front row (L to R):**

Xiaomei Yu, Sikorsky Aircraft Corporation, Weilong Zhang, UTRC

Promila Bhatia,, Pratt & Whitney

## **Other UTRC Team members:**

Sara Arsenault  
Tom Garosshen  
Steve Gore  
Foster Lamm  
Vince Nardone  
Xia Tang

## **Other P&W team Members:**

Thomas Hanlon  
Camelia Galos  
Alex Korzh  
Nathalie Laurent  
Ray Martina  
John Putnam  
Charlie Watson

## **3M Team Members:**

Lance Chen  
Eric Forbes  
Michael S. Newman (Primary Contact)  
Dmitriy Salinkov  
Pete Steinhagen

